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THE DIELECTRIC PROPERTIES OF ESTER GUM

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ABSTRACT. The dielectric properties of ester gum have been measured over a wide range of temperature and frequency viz , from 22°C to 140°C and from 400 cycles per second to 300 kc/s. The resin shows characteristic polar properties and the region of anomalous dispersion extends over a wide range The maximum value of dielectric loss at any frequency is less than that demanded by Debye's theory and the ϵ''/ϵ''_m plot against f/f_m gives a much blunter curve than the theoretical one indicating thereby a distributed relaxation time of the orientating dipoles. The radius of the rotating unit, calculated from data reported here and the melt-viscosity data published earlier, gives an average value of 1.5 Å only, which is the same as that of a hydroxyl group. From the consideration of composition of ester gum it has been postulated that the dielectric loss of this resin is mainly due to the presence of glyceryl mono- and di-abietates in this resin.

INTRODUCTION

Resins in general are quite different from both crystalline solids and ordinary liquids; in their bulk mechanical properties they resemble solids, while as far as details of molecular mechanics are concerned they have many of the properties of liquids. According to their behaviour towards heat treatment, resins may have two other classifications, viz, (a) the thermoplastics, which soften on heating and solidify on cooling, the process being reversible and (b) the thermo-setting resins, which sometimes soften on heating but solidify on continued heating, the process being irreversible These two types of behaviour are believed to be due to the difference in their molecular structure The thermoplastic resins usually have a long chain molecular structure, whereas the thermo-setting ones have a cross-linked structure Hence the molecules of a thermoplastic resin are in a position to respond more freely to impressed external forces such as heat or electric field than those of a thermo-hardening type.

According to Debye's dipole theory, all polar substances are expected to show anomalous dispersion and the accompanying dielectric loss somewhere in the frequency range determined by the size and shape of dipoles and the inner friction coefficient, which again depends upon temperature. Important information regarding their physical structure may thus be obtained from a study of their behaviour in an alternating electric field under varying conditions of temperature and frequency. Debye's simple dipole theory can very well account for such dispersion in case of substances having smaller molecules with single relaxation

time and yields important data regarding their physical structure. But sometimes such direct and quantitative application of Debye's equations becomes difficult in the case of a substance having large molecules with distributed relaxation time, as in the case of a complex polar resin whose polar groups may not be free but anchored to a common chain It has been observed that in many such cases these groups only orient with the alternating field instead of the whole molecule.

Chemically speaking ester gum is the glycerol ester of rosin acids about 98% of which is abietic acid. It is a thermoplastic resin having a softening range of temperature near about 79°C. Ester gum is largely used in various industries although wood rosin is considered as an inferior resin owing to its high acid value Its molecular weight is about 900, hence although the molecule is small compared to most polymeric resins, it may be sufficiently large for the quantitative application of Debye's equations. It is, therefore, of considerable interest to study the dielectric properties of this thermoplastic resin with a view to getting an idea of the size of the rotating unit.

THEORETICAL

The dielectric properties of a substance which exhibits the phenomenon of absorption or dielectric loss may be expressed in terms of a real and an imaginary part of the complex dielectric constant, viz ,

$$\epsilon = \epsilon' - j\epsilon''$$

where ϵ = the complex dielectric constant,

ϵ' = the real or ordinary dielectric constant or permittivity,

and ϵ'' = the imaginary part or the dielectric loss factor

The relation between the dielectric loss factor ϵ'' and the dielectric constant ϵ' is generally expressed as

$$\epsilon'' = \epsilon' \cos \phi$$

ϕ being the phase angle by which the current vector leads the voltage vector across a condenser filled with the given dielectric material. In the case of a perfect dielectric this angle would be 90°. The angle δ which measures the lag of the phase angle from 90°, is called the loss angle and is usually very small in case of dielectric materials.

Since δ is very small and $\phi + \delta = 90°$, we have

$$\epsilon'' = \epsilon' \cos \phi = \epsilon' \sin \delta = \epsilon' \tan \delta$$

where tan δ is called the power factor of the condenser. The dielectric constant ϵ' and the power factor tan δ of a condenser may be determined in the usual manner and the dielectric loss ϵ'' may be computed.

EXPERIMENTAL

Apparatus : For the measurements of permittivity and power factor of ester gum a General Radio type 716-C capacitance bridge was used. The generator was a G.R. type 1330-A bridge oscillator and the detector-amplifier was a G.R. type 1212-A unit null-detector having a suitable gain of amplification over the range of frequency investigated.

Throughout this investigation a vertical type parallel plate condenser was used. The metal plates were fixed on a fused quartz plate. The condenser could be placed inside a small beaker containing the material to be investigated upon in the liquid state. This vertical type condenser was preferred to the horizontal type as the adherent air bubbles could easily escape from the former. The details of construction of this type of condenser has been described previously (Bhattacharya, 1944).

Method of Procedure · Preliminary tests were made on the condenser as regards the constancy of its value and was found to be quite satisfactory. The condenser was placed inside a completely shielded enclosure and leads were taken out through coaxially shielded quartz tube The outer shield and one set of the condenser plates were connected to the ground terminal of the bridge which was earthed. Keeping the condenser in this position its air-capacity was determined by using chemically pure benzene up to a certain mark on the beaker. Hence, by measuring the capacity of the test cell filled up to the said mark with the material its dielectric constant could be determined.

Ester gum was melted in a crucible and poured in the beaker and kept inside a hot air oven alongside the condenser to allow the dissolved air bubbles to rise gradually up to the surface. The hot condenser was then slowly put in the molten ester gum taking care to avoid adherent air bubbles. The temperature of the oven was then slowly brought down to the room temperature. A thin cork pad in the form of a ring was placed between the rim of the beaker and the quartz plate in order to avoid undue strain during the setting of the resin on cooling. The temperature of the oil bath was controlled by a thermostat within $\pm$ 0.2°C. Measurement of d.c. resistivity was carried out using the same condenser. The details of this measurement have already appeared (Sen and Bhattacharya, 1957).

DISCUSSION

In figures 1, 2 and 3, the power factor tan δ, the dielectric constant ϵ' and the dielectric loss ϵ'' have been plotted as respective functions of temperature. All these curves can be explained in terms of orientation of polar molecules in the light of Debye's theory. According to Debye the dielectric loss is caused by the orientation of polar molecules, when placed in an alternating electric field, against an

RESULTS

TABLE I

Dielectric constant—temperature data.

Temperature in °C	Dielectric constant ε' at						
	400 c/s.	1 kc/s.	5 kc/s.	10 kc/s.	50 kc/s.	100 kc/s	300 kc/s.
22°	2 717	2 714	2 708	2 704	2.702	2 698	2 692
30°	2 719	2.719	2 712	2 712	2 707	2 702	2 700
40°	2 748	2 745	2 733	2 738	2 733	2.732	2 727
50°	2.790	2 781	2 775	2 771	2 763	2.763	2 753
60°	2 831	2 816	2 798	2 790	2 779	2.775	2 771
70°	2.969	2 900	2 836	2.827	2 805	2 796	2.790
80°	3 360	3 154	2 954	2 917	2 851	2 829	2 805
90°	3 748	3 569	3 310	3 119	2 962	2.910	2 854
100°	3 858	3.783	3.616	3 455	3 175	3.073	2 949
110°	3 848	3.810	3 681	3 584	3 362	3.300	3 054
120°	3.835	3.787	3.768	3 740	3 619	3.489	3.323
130°	3 810	3 796	3 784	3 773	3 709	3 637	3.512
140°	3.777	3 773	3.766	3 755	3 733	3.702	3 618

TABLE II

Power factor—temperature data

Temperature in °C	Power factor tan δ (corrected for d.c. conductivity) at						
	400 c/s.	1 kc/s	5 kc/s.	10 kc/s.	50 kc/s	100 kc/s.	300 kc/s.
22°	0 0018	0 0018	0 0014	0 0014	0.0018	0 0020	0.0027
30°	0 0017	0 0017	0 0013	0.0013	0 0017	0 0019	0.0027
40°	0 0012	0 0014	0.0012	0 0012	0 0016	0.0018	0 0027
50°	0.0036	0 0030	0.0022	0 0020	0 0020	0.0022	0 0033
60°	0 0105	0 0077	0 0052	0.0043	0 0031	0.0031	0 0039
70°	0.0388	0 0240	0.0132	0 0105	0 0067	0.0060	0.0057
80°	0.0800	0.0600	0 0370	0.0295	0.0170	0 0140	0.0111
90°	0.0644	0.0685	0 0755	0.0577	0 0380	0.0320	0 0222
100°	0.0254	0 0370	0 0581	0 0720	0 0625	0 0585	0.0427
110°	0.0099	0.0173	0 0350	0 0405	0.0680	0 0750	0.0615
120°	0.0033	0 0057	0.0169	0.0229	0 0515	0.0662	0.0741
130°	0.0011	0 0025	0.0079	0 0123	0 0314	0 0465	0.0660
140°	0.0018	0.0010	0 0040	0 0058	0 0171	0.0267	0.0480

TABLE III

Dielectric loss-temperature data

Temperature in °C	Dielectric loss ε″ (corrected for d.c. conductivity) at						
	400 c/s	1 kc/s	5 kc/s.	10 kc/s.	50 kc/s.	100 kc/s	300 kc/s.
22°	0.0049	0 0050	0 0038	0.0038	0.0480	0.0054	0.0073
30°	0 0046	0.0046	0 0034	0.0035	0.0047	0.0051	0.0073
40°	0 0033	0.0038	0.0033	0 0033	0.0046	0.0049	0.0074
50°	0.0101	0.0085	0.0062	0.0055	0 0055	0 0061	0 0091
60°	0.0297	0 0216	0 0147	0.0120	0 0086	0 0087	0.0108
70°	0 1152	0 0696	0 0376	0 0297	0.0189	0 0168	0 0159
80°	0 2669	0 1892	0 1093	0 0861	0.0485	0 0396	0.0311
90°	0.2414	0 2440	0.2499	0.1800	0.1126	0.0931	0.0634
100°	0.0980	0.1400	0 2100	0 2488	0.1985	0.1798	0.1261
110°	0 0377	0.0659	0.1288	0.1451	0.2310	0 2429	0.1878
120°	0.0127	0.0216	0.0636	0.0858	0.1864	0 2310	0 2462
130°	0.0042	0.0097	0.0300	0.0466	0.1166	0.1690	0 2317
140°	0.0067	0.0038	0.0152	0 2174	0.0640	0.0988	0.1737

internal frictional force or viscosity. At lower temperature, when the substance is more or less in a solid state, the inner frictional force or viscosity is so great that the dipoles are unable to orient themselves in response to the impressed alternating

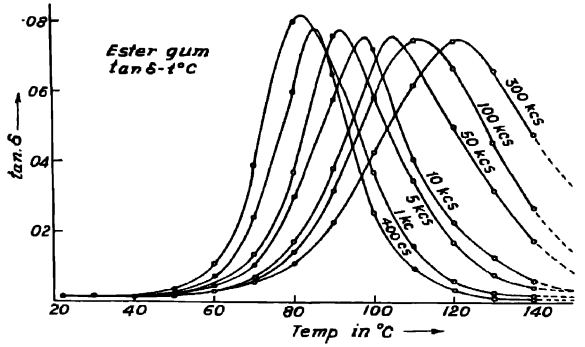
Ester gum
tan δ-t°C
tan δ
·08
06
04
02
20
40
60
80
100
120
140
Temp in °C
300 kcs
100 kcs
50 kcs
10 kcs
5 kcs
1kc
400 cs

Fig. 1

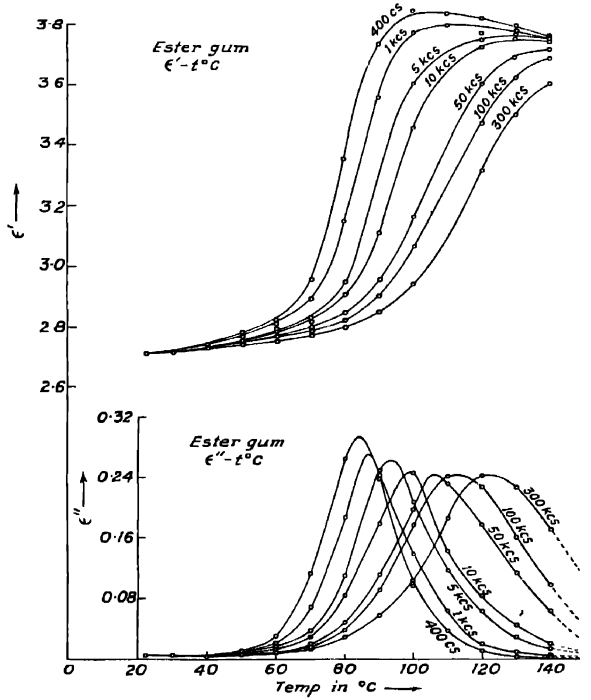
Ester gum
ε'-t°C
ε'
3·8
3·6
3·4
3·2
3·0
2·8
2·6
400 cs
1kcs
5 kcs
10 kcs
50 kcs
100 kcs
300 kcs
Ester gum
ε''-t°C
ε''
0·32
0·24
0·16
0·08
0
20
40
60
80
100
120
140
Temp in °C

Fig. 2 & 3.

field as if they are "frozen in". Consequently, the dielectric loss and the power factor are low The value of the dielectric constant is also low and is mainly due to the electronic polarisation as any contribution from dipole polarisation is almost nil. At very high temperatures thermal agitation tends to produce a random distribution of dipoles thereby making a very few dipoles available to orient themselves in response to the field And even those few dipoles that orient absorb little energy from the field as the resistance to such orientation is very small owing to the logarithmic decrease of viscosity with temperature. Thus at high temperatures, too, the loss and the power factor are low. Between these two extremes there will be states at which the dipoles can respond more or less freely to the alternations of the impressed field against the opposing forces of both the internal viscous forces of the material as well as those due to thermal agitation With the increase of temperature the forces due to thermal agitation increase, whereas those due to viscosity decrease. At any temperature, therefore, the loss is determined by the frequency of the alternating field as well as the viscosity of the substance and the size and shape of the dipoles giving the characteristic relaxation time τ

As the softening point of the substance is approached with the increase of temperature, the internal viscosity decreases rapidly and more and more polarisation takes owing to increased participation of the "frozen in" dipoles in the orientation, resulting in a steep rise in the value of the dielectric constant. Then the dielectric constant tends towards a maximum indicating a liquid state with the maximum number of oriented dipoles and the high value of the dielectric constant approaches ϵ_0', the "static value" of the substance at the particular temperature. With a further rise in temperature the opposing forces due to thermal agitation predominate and so the number of oriented dipoles diminish, resulting in a lower value of the dielectric constant It may be seen from figure 2 that this stooping portion of the dielectric constant-temperature curve was obtained for the frequencies, 400 c/s and 1000 c/s only while those for other frequencies seem to lie at temperatures higher than the range of investigation.

Now, for a given substance the amount of dipole polarisation depends upon the relative values of relaxation time τ and the period of the alternating field $2\pi/\omega$. When this period is very small *i.e.* for very high frequencies compared with $1/\tau$, the dipole polarisation is negligible, hence both the dielectric constant and the dielectric loss are low. This may be seen from figures 2 and 3. When the period of the field is large compared with τ, complete polarisation takes place in each half of the cycle and the dielectric constant approaches the maximum value. Because of the low value of τ compared with the period of the field, orientation also does not lag behind the field alternations, thus resulting in a low loss. The change of the dielectric constant from a low value to a large one occurs in the region in which the half period of the applied field is of the same order as

the relaxation time. Again, in this region polarisation can not keep pace with the field alternations and it lags appreciably behind the field, with the result that both dielectric loss and power factor approaches maximum values. It may be noted from figures 2 and 3 that the peak of any loss curve corresponds to a temperature at which the maximum variation of dielectric constant takes place in the corresponding ϵ'—temperature curve.

As with the increase of temperature relaxation time decreases, it follows that the dielectric loss peaks corresponding to different frequencies would occur at higher and higher temperatures as the frequency is increased. This may be seen from figure 3. At the frequency of 400 c/s the maximum dielectric loss takes place at 84°C while for the frequencies of 1, 5, 10 and 50 kc/s the peaks occur at 87°C, 94°C, 99°C and 106°C respectively For 100 kc/s and 300 kc/s, the peaks, which are blunter than the previous ones, occur at still higher temperatures viz., at 112°C and 122°C respectively. Thus within the above frequency band the peaks spread through a range of about 38°C. From the curves it may again be noted that the value of the maximum loss ϵ''_m of each curve increases as we proceed towards lower temperatures Thus ϵ''_m for the curve corresponding to 400 c/s is 0.296 the maximum occurring at 84°C, whereas ϵ''_m for 300 kc/s is only 0.246 at 122°C.

It is quite appparent that all the curves given above are in qualitative agreement with the expected behaviour of polar molecules according to Debye's theory. But the electrical properties of polar systems containing large molecules differ markedly from those in which the molecules are small. The properties of the latter are well accounted for by Debye's theory in which the fundamental assumption is the single relaxation time and the small size and simple shape of the rotator.

But in the case of a polar substance having large molecules, such as polar polymers, polar groups sometimes are attached to a common chain or to other polar groups attached to the chain. The different possible configurations of the chain and their random distribution under thermal agitation give rise to a band of distributed relaxation times for the entire molecule instead of a single one as in the case of a simple polar molecule (Fuoss and Kirkwood, 1941). Now from theoretical considerations (Wagner, 1913 and Yager, 1936) it has been shown that the characteristic difference between a polymeric system and a system describable in terms of a single relaxation time is revealed by a diminution in the value of the maximum loss ϵ''_m from that demanded by Debye's equation as well as by the widening of the dispersion band.

The maximum value of the dielectric loss of a polar liquid at any temperature, according to Debye's theory, can be represented as

$$\epsilon''_m = \frac{\epsilon_0' - \epsilon_\infty'}{2}$$

where ϵ_m'' = the maximum value of the loss,

ϵ_0' = the static dielectric constant at the particular temperature,

and ϵ_∞' = the value of the dielectric constant at very high froquencies.

For ester gum, the value of ϵ_0' at 100°C can be estimated from figure 4 to be 3.89 and that of ϵ_∞' 2.79. Hence on the basis of Debye's relation the value of the maximum loss at 100°C should have been 0.55. But the experimental value, as

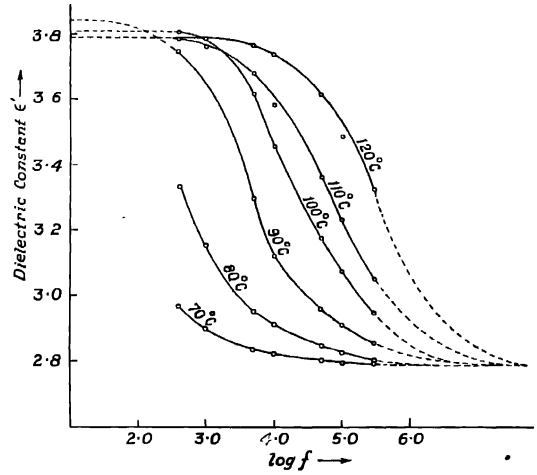

Fig 4.

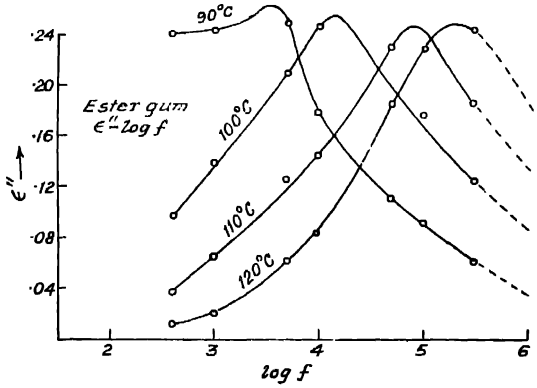

Fig 5

can be seen from figure 5, is 0 256 which is only half of the theoretical value. Thus the quantitative application of Debye's relation is found to be invalid in this case.

It may be seen from ϵ'-frequency and ϵ''-frequency curves of figures 4 and 5 that both the regions of dispersion as well as of absorption extend over a wide range of frequency not less than 6 or 7 decades. The values of ϵ''/ϵ_m'' for ester gum, obtained from the 100°C data of figure 5, are plotted against log f/f_m and the resulting curve is shown in figure 6. The Debye curve is also shown in the same

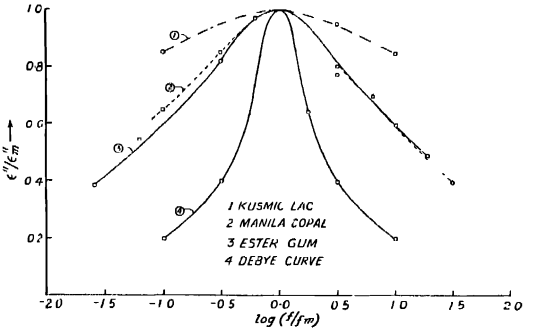

Fig. 6.

figure for the sake of comparison and it may be seen that the curve for ester gum is much blunter than the theoretical curve Similar curves for several other resins are also represented in figure 6 for the sake of comparison. It may be seen that the curve for ester gum almost coincides with that for Manila copal obtained previously by one of us (Bhattacharya, 1946). Thus the effects of distributed relaxation times are quite evident in the case of ester gum by the blunter shape of the absorption curve as well as by the wide departure of the observed value of the maximum loss from the calculated one.

As stated previously, the phenomenon of dielectric loss of polar materials caused by the orientation of dipoles in an alternating electric field, is, according to Debye, a relaxation mechanism controlled by an internal frictional force. The relation between the relaxation time and the internal frictional torque encountered by a dipole in an alternating field, is

$$\tau = \frac{\xi}{2kT}$$

where τ = relaxation time, ξ = frictional torque, k = Boltzmann constant, and T = absolute temperature.

In the case of a liquid where a spherical shape of the rotator can be assumed, ξ can be written as equal to $8\pi\eta a^3$, according to Stoke's law, so that

$$\tau = \frac{4\pi\eta a^3}{kT} \qquad \ldots \quad (1)$$

where η = coefficient of viscosity and a = radius of the rotator.

Now τ can be calculated from another relation due to Debye, viz.,

$$\omega\tau = \frac{\epsilon_\alpha' + 2}{\epsilon_0' + 2} \qquad (2)$$

at a temperature where the dielectric loss is maximum for any frequency and ϵ_0' and ϵ_∞' are the static dielectric constant and the dielectric constant at very high frequencies respectively at that temperature.

From the last two relations it is quite apparent that if the values of η and τ for the temperature at which the maximum dielectric loss takes place for a particular frequency are known, the radius of the dipole unit a can be determined The coefficient of viscosity of this resin has already been determined over the range of temperature investigated (Sen and Bhattacharya, 1957) The relaxation time τ for a particular temperature can be determined from the ϵ'—log f curve using relation (2). The results of this computation are shown in Table IV below.

TABLE IV.

Frequency (in kc/s.)	T_m (Temp. in °C at which ϵ_m'' occurs)	ϵ_0' (at T_m)	ϵ'_∞	τ (Relaxation time in sec)	log η (at T_m)	a (in Å)
1	87°	3.850	2 790	1.304×10^{-4}	5 26	1 41
5	94°	3.860	2.790	$2\ 605\times10^{-5}$	4.54	1.44
10	99°	3.890	2 790	$1\ 294\times10^{-5}$	4 13	1.58
50	106°	3 870	2.790	2.597×10^{-6}	3.49	1.52
100	112°	3.860	2.790	1.301×10^{-6}	3.07	1.67

From Table IV it may be clearly seen that the radii of the rotator units, although computed from various data corresponding to different frequencies, are in close agreement and they all lie within a narrow region around the most probable value of 1.5 Å.

The smallness of these values is one of their most striking features. From the molecular structure of abietic acid, as given by Ruzicka and his co-workers (1932, 1933), it is quite evident that ester gum, which is mainly a glycerol ester of abietic

acid, can not in any possibility have such a small dimension if we assume the whole molecule to rotate in response to the alternating field. On the other hand, the value of the radius of OH group has been fairly established from X-ray and other methods as having 1.5 Å. The exact coincidence of these two values suggests that perhaps it is the hydroxyl group in the ester gum molecule which mainly participates in the orientation when placed in an alternating field instead of the whole molecule.

Hartshorn and co-workers (1940) arrived at a similar conclusion in case of some synthetic phenolic resins. One of us (Bhattacharya, 1944) also demonstrated that in case of several lac resins the rotator unit was the hydroxyl group.

Ester gum is obtained commercially by the esterification with glycerol of wood rosin about 98% of which is abietic acid. Abietic acid molecule contains only one —COOH group, according to the structure suggested by Ruzicka and co-workers (1932, 1933). Glycerol, being a trihydric alcohol, would require three molecules of abietic acid for complete esterification to form glyceryl tri-abietate and no free hydroxyl group is expected in this ester. Doubts naturally arise as to the propriety of identifying the rotating unit in the ester gum molecule with hydroxyl group. But Ellis (1935) has pointed out that complete esterification is very difficult in the formation of ester gum from glycerol and abietic acid and in usual practice ester gum obtained consists of glyceryl tri-abietate together with some amounts of mono- and di-abietates. In the glyceryl mono- or di-abietates one or two of the three hydroxyl groups of glycerol remain unesterified. Perhaps it is these unesterified hydroxyl groups which contribute towards the dipole orientation and their dimensions have been obtained in the calculation of the rotator size.

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